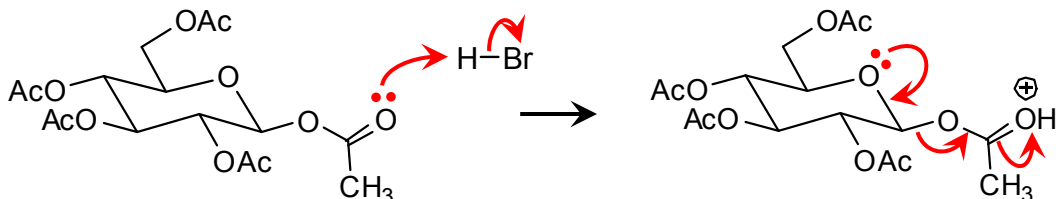
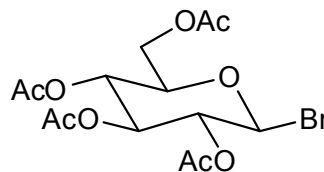
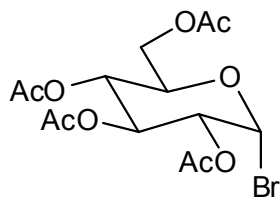
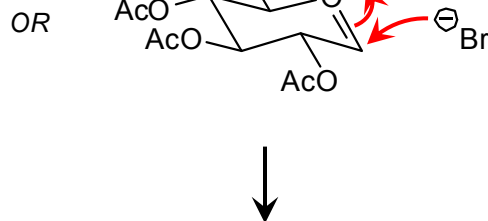
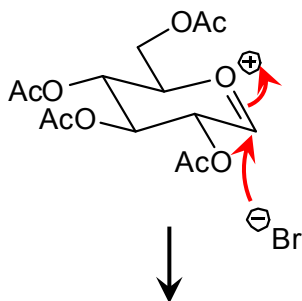


Workshop 21 Solutions
Mechanisms of Glycolysis

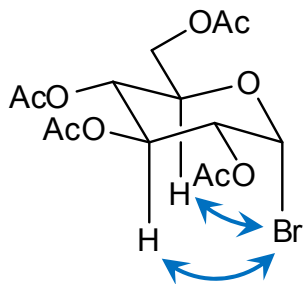
1. a)



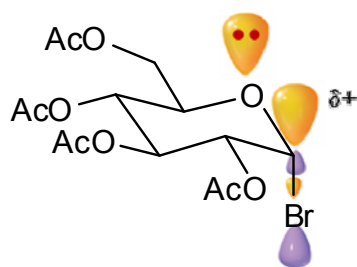
The double bond here is actually flat, but I drew it twisted to help illustrate how the products are formed.



b)

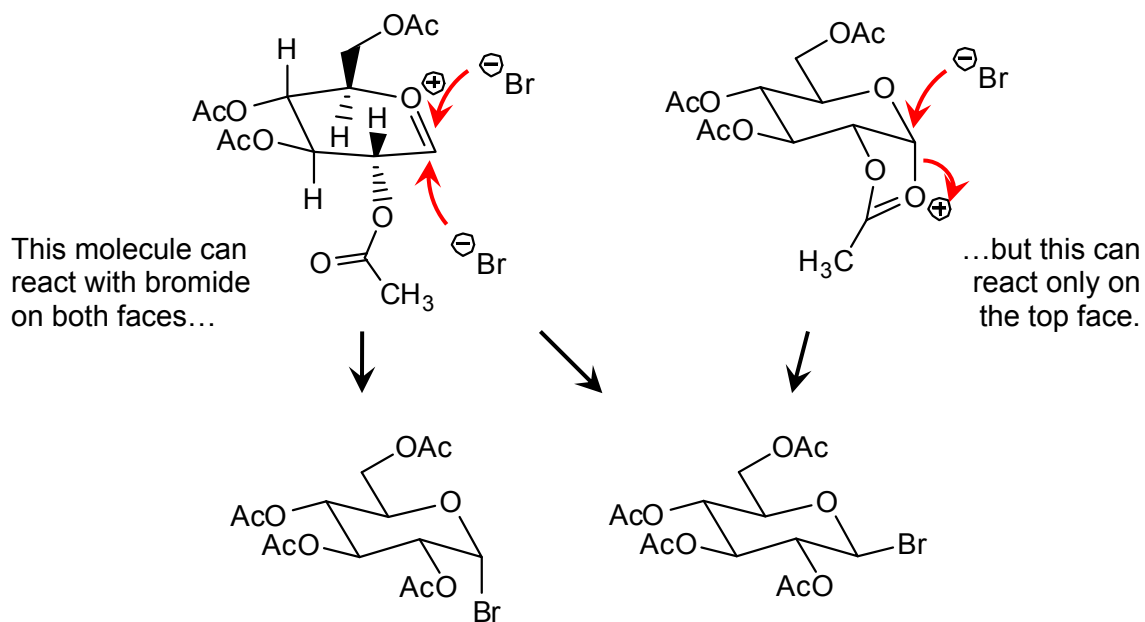


1,3-diaxial interactions
favor β -anomer



anomeric effect
favors α -anomer

- c) The α -anomer is stabilized by the anomeric effect, and so is the transition state leading to the α -anomer (though to a lesser extent). So if the anomeric effect predominates, in this system, the α -anomer should be favored. The α -anomer is destabilized by steric, 1,3-diaxial interactions between the axial $-\text{Br}$ and the ring. The β -anomer doesn't have this problem, and so if steric effects predominate, the β -anomer should be favored.
- d) Hammond Postulate would argue that the same effects that influence the products will also influence transition-state energies, such that the thermodynamic product is also the kinetic product. Here, however, kinetic control (low temperature, short time) gives a different product than thermodynamic control (long time, higher temperature). Hammond Postulate must not hold here, meaning that there must be something else going on in the reaction to explain the product distribution.
- e) If the acetate group attaches to the bottom face of the double bond, that face is no longer available for approach of a nucleophile. So bromide anion can only approach from the top face:



This pattern of reactivity doesn't change the relative stabilities of α - and β -anomers, and it is still true that the α -anomer is stabilized by the anomeric effect. But the group attached to the bottom face of the ring blocks the approach of the bromide, and kinetically inhibits the formation of the more stable α -anomer.